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Evaluation of Selected Gaseous Halocarbons for Use in Source Test Performance Audits

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16. ABSTRACT

A repository of 38 gaseous organic compounds in compressed gas cylinders has been established by the U.S. Environmental Protection Agency. This repository was established to provide standards for source test performance audits, that is, quantitative quality assurance tests. Among these compounds are ten halogenated organic species, which are the focus of this study. These compounds are: chloroform, 1,2-dichloroethlene, trichloroethylene, 1,1-dichloroethylene, perchloroethylene, vinyl chloride, methylene chloride, carbon tetrachloride, freon 113, and 1,1,1-trichloroethane. Stability studies of all ten compounds have been performed to determine the feasibility of using them as performance audit standards. Results indicate that all of the halocarbons tested are adequately stable to be used as reliable audit standards. Also included are source test performance audit results using these halocarbons.

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EVALUATION OF SELECTED GASEOUS HALOCARBONS FOR USE IN SOURCE TEST PERFORMANCE AUDITS

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A repository of 38 gaseous organic compounds in compressed gas cylinders has been established by the U. S. Environmental Protection Agency (USEPA). This repository was established to provide standards for source test performance audits, that is, quantitative quality assurance tests. Among these compounds are ten halogenated organic species, which are the focus of this paper.

Stability studies of all ten compounds have been performed to determine the feasibility of using them as performance audit standards. Results indicate that all of the halocarbons tested are adequately stable to be used as reliable audit standards.

Subsequent to completion of stability studies, four of the ten halocarbons were used in source test performance audits. Results are available at this time for two of the four compounds; the results show agreement within 10% of the concentrations previously established by RTI.

EVALUATION OF SELECTED GASEOUS HALOCARBONS FOR USE IN SOURCE TEST PERFORMANCE AUDITS

INTRODUCTION

The application of quality assurance practices is important in the generation of high quality environmental data. The performance audit, which is one such practice, involves the analysis of standard samples whose concentrations have been reliably established. When measured concurrently with a source emission sample, the performance audit sample provides a measure of the analysis accuracy. This accuracy determination is used in setting standards and for compliance testing after emission standards have been promulgated. When it is demonstrated that performance audit materials are stable in the 5 to 20 ppm concentration range, a performance audit can be included as a part of the established test method.

The Quality Assurance Division of EPA's Environmental Monitoring Systems Laboratory - RTP has a program to supply accurate quality assurance materials for use when conducting environmental measurements. While participating in this program and under contract to the U.S. Environmental Protection Agency (USEPA), the Research Triangle Institute (RTI) is conducting a performance audit program utilizing an extensive repository of gaseous compounds. These compounds are used in audits as designated by EPA Project Officers. The repository currently contains 38 different compounds selected on the basis of anticipated needs of EPA's Office of Air Quality Planning and Standards. A list of these compounds is shown in Table I.

Among these 38 compounds are 10 halogenated organic species. Five of these 10 compounds are available in two concentration ranges. The low concentration range, 5 to 20 parts per million, simulates possible emission standard levels. The high concentration range, 50 to 700 parts per million, simulates expected source emission levels. The remaining 5 compounds are available only in the low concentration range. The balance gas for all gas mixtures is nitrogen. A description of these halocarbon audit standards is given in Table II.

These gaseous compounds are purchased from commercial suppliers as dilute mixtures in compressed gas cylinders. A cylinder, together with a suitable gas delivery system, is used directly in the performance audit; dilution of the cylinder contents is not performed.

Before being used as an audit standard, each cylinder contents undergoes a series of analyses at RTI. The cylinder contents are analyzed after initial receipt from the manufacturer to check the reported concentrations of the test compound. The cylinder contents are then analyzed periodically over the course of a year to estimate the compound stability. All concentration measurements are made using gas chromatography (GC) with flame ionization detection.

EXPERIMENTAL METHODS

Instrumentation

Analyses were performed with (1) a Perkin-Elmer Model 3920-B gas chromatograph with a flame ionization detector or (2) a Perkin-Elmer Sigma 4 gas chromatograph with a flame ionization detector. A fixed sample volume of each gas in a sample loop was injected onto the gas chromatographic column through a six-port sampling valve. After separation of the halocarbon from nitrogen, an FID response was produced and electronically integrated. GC conditions for analyses have been previously described in a separate publication.[1]

Standardization and Measurement

Calibration standards were prepared from pure compounds. The calibration standard preparation technique used for the majority of the halocarbons consisted of syringe injection of known quantities of the pure organic compound into an evacuated glass bulb of approximately 2 liters in volume. The bulb was then filled with pure nitrogen and its final pressure measured with a Heise bourdon tube compound gauge. The concentration of the halocarbon standard was calculated using the ideal gas law. Additional dilution of the sample was accomplished by depressurization and repressurization with pure nitrogen to achieve the desired concentration.

Known concentrations of vinyl chloride in nitrogen were prepared using a permeation tube/dilution system. The tube was placed in a temperature controlled chamber with pure nitrogen passing over it. By varying the flow rate of nitrogen across the tube or by further dilution downstream with pure nitrogen, different concentrations of vinyl chloride could be generated.

A multi-point standard curve was generated for those compounds which exhibited a linear FID response. For those which showed evidence of non-linearity, a single point calibration using a standard concentration near that of the expected concentration was used. This avoids the bias which can be introduced with a least squares fit of a non-linear FID response.

Analytical Quality Control

During the course of development of analytical procedures for measuring the halocarbon concentrations, several sources of possible analytical error were noted. These were controlled by practicing suitable quality control measures. These measures included the following:

(1) In the calculation of calibration standard concentrations, the total volume of the glass bulb plus the bourdon tube volume in the Heise gauge must be used.

(2) Higher accuracy in the preparation of standards is achieved using a minimum of 10 microliters of pure organic compound and performing dilutions rather than attempting to accurately syringe one or two microliters.

(3) It was necessary to heat the syringe during delivery of some of the organic liquids to the glass bulb to assure complete transfer.

(4) Heating of the sample loop and sampling valve was necessary during analysis of carbon tetrachloride in order to produce good precision in the responses to repeated injections of a sample.

(5) Decomposition of 1,1,1-trichloroethane was caused by passage of the sample from the sampling valve through a heated on-column injector and onto the column. This was alleviated by by-passing the injector with a length of 1/16 in. OD stainless steel tubing.

(6) A bias in the analysis of low concentrations of halocarbon was produced when a least squares fit of the detector response to high concentration standards was used. This is the result of non-linear detector response at low concentrations. This bias was avoided by using a single calibration standard close in concentration to the cylinder gas or by bracketing the cylinder gas concentration with two standards.

RESULTS AND DISCUSSION

Performance Audits

As stated earlier, RTI supplies repository cylinders for audits upon request from the EPA Project Officers. These requests are sometimes directed through the EPA from state and local government agencies or from their contractors. The contractors must, however, be performing source emission tests on behalf of the EPA or one of these other agencies to qualify for the performance audit. When a request is received, the contents of the cylinders to be shipped are analyzed, the cylinder pressures are measured, and the cylinders are shipped by truck to the audit site. General instructions for performance of the audit are included with the cylinders. The audit results are reported to the EPA or the requesting agency audit coordinator.

To date, 95 performance audits have been completed. Of these 95, six requests have been received for the halogenated organic compounds. The results of the halogenated organic performance audits are shown in Table III. As noted previously, high and low level concentrations were included in most audits. Also, as shown in Table III, the audit materials were not analyzed by the client for unknown reasons for four out of the six audits. However, for the audit materials analyzed, the audit results ranged from a -8.7 percent bias for a trichloroethylene measurement to +6.0 percent bias for a 1,2-dichloroethane measurement.

The principal effects of these audits have been (1) to assure all concerned that analyses are being performed properly and/or to uncover problems that could be corrected and (2) to document the accuracy of the actual source emission test analysis.

Stability Studies

The data collected over time from the measurement of cylinder concentrations were used to estimate the stabilities of the halocarbon gases. Cylinder gas stability data are important for several reasons. First, audit materials used by EPA must be stable to be considered as reliable audit standards. Second, if organic gases in cylinders are stable, other investigators may more readily use cylinder gases as calibration standards and/or quality control check samples. Finally, if cylinder contents are stable, future EPA regulations could include performance audits as a means of assessing the accuracy of the analysis data.

The term stability, as pertains to this study of gaseous compounds, is defined as the change in concentration with time for a given cylinder at a specified concentration level. Analyses of cylinder contents were performed as soon after arrival as possible, and then at periodic intervals over the course of the stability study. Additional analyses were performed on individual cylinders prior to use in an audit. These data were also used in the estimate of the stability.

Statistical Analysis. The statistical analysis was primarily directed at assessing the changes in concentration over time. This assessment was performed through application of statistical models. The first model used allows pooling of data for all cylinders containing the same compound and thus was used for those compounds in which several cylinders were analyzed. These were chloroform, 1,2-dichloroethane, trichloroethylene, 1,1-dichloroethylene, and perchloroethylene. The model is:

$$Y_{ix}^{(C)} = {}_{i}^{(C)} + b^{(C)}X + e_{ix}^{(C)} \qquad \text{Model 1}$$

where

$Y_{ix}^{(C)}$ = concentration (ppm) for compound C for cylinder i on day X

$\mu_i^{(C)}$ = intercept for compound C for cylinder i, i.e., initial concentration.

$b^{(C)}$ = slope for compound C, i.e., change in concentration with change in time.

X = time in days

$e_{ix}^{(C)}$ = a statistical error term; these terms are assumed to be independent, identically distributed, random variables for all cylinders.

For a second group of compounds, each contained in a single cylinder, data were collected from replicate measurements using the same calibration and also from measurements using separate calibrations on the same day. These compounds were methylene chloride, carbon

tetrachloride, Freon 113, and 1,1,1-trichloroethane. Since there were multiple measurements on each day with each calibration, and measurements with two calibrations on at least one day for each of the four compounds, then the analytical errors could be estimated. The calibration and measurement errors were estimated using the following model:

$$Y_{tij}^{(C)} = \mu^{(C)} + B^{(C)} t + C_i^{(C)}(t) + e_{tij}^{(C)} \qquad \text{Model 2}$$

where

$Y_{tij}^{(C)}$ = the concentration of compound C for the j^{th} determination based on the i^{th} calibration on day t.

$\mu^{(C)}$ = intercept for compound C, i.e., concentration at time zero.

$B^{(C)}$ = Effect associated with time t for compound C.

t = time in days

$C_i^{(C)}(t)$ = a random error associated with the i^{th} calibration for compound C for day t. These terms are assumed to be independent, normal variables with mean zero and calibration error as variance.

$e_{tij}^{(C)}$ = a statistical error term

The calibration error for the four compounds is shown in Table IV along with the measurement error (random error from replicate measurement using the same calibration). The magnitude of the calibration error is notably larger than the measurement error for all of the compounds except methylene chloride.

The slopes for the four compounds were estimated using the model as follows:

$$Y_{tc}^{(C)} = \mu^{(C)} + B^{(C)} t + e_{tc}^{(C)} \qquad \text{Model 3}$$

where

$Y_{tc}^{(C)}$ = Mean value of all determinations for compound C based on calibration C.

$\mu^{(C)}$ = Intercept for Compound C, i.e., concentration at time zero.

$B^{(C)}$ = the slope for Compound C

t = time in days

$e_{tc}^{(C)}$ = an error term

The statistical test of significance for slope was done using regression analyses. Results of statistical analysis using these models are shown in Table V and indicate that the change in concentration with time is not statistically significant for the nine compounds tested.

For vinyl chloride, insufficient data have been collected to date to perform a statistical analysis using either of the above models. As an estimate of the vinyl chloride stability, a least squares fit of the data for each cylinder was performed with X as days and Y as ppm. The percent change per month is then calculated by:

$$\text{per cent change per month} = m/b \times 100 \times 30 \text{ days} \qquad (1)$$

where m = slope
b = y intercept

The estimates of instability for nine cylinders containing vinyl chloride ranged from 0.01% per month to 0.71% per month with an average value of 0.36% per month. This indicates the possibility for some instability but more data are necessary to perform a detailed statistical analysis.

CONCLUSIONS AND RECOMMENDATIONS

The stability data obtained to date for 10 halocarbons indicate that all of them are adequately stable for use in source test performance audits. Measurement and calibration errors in the analysis of some of the compounds were found to be somewhat smaller than the total variation in the compound concentrations over time. This suggests unknown sources of analysis error, assuming that the compounds are stable.

The compressed cylinder gases of halocarbons can be used successfully for performance audits to assess and document the accuracy of actual source emission analysis. Hence, it is recommended that a performance audit using compressed cylinder gases of halocarbons be conducted during future source emission analyses as a routine quality assurance procedure. Any federal, state, and local agencies and their contractors planning source emission tests for organics may request a performance audit by contacting the EPA Regional Quality Assurance Management Office or EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, at Research Triangle Park, North Carolina.

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REFERENCES

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Table I. Organic Gases in Performance Audit Repository

Acrolein	Hexane
Acrylonitrile	Hydrogen Sulfide
Allyl Chloride	Meta-Xylene
Benzene	Methane/Ethane
1,3-Butadiene	Methanol
Carbon Disulfide	Methyl Acetate
Carbon Tetrachloride	Methyl Chloroform
Carbonyl Sulfide	Methylene Chloride
Chlorobenzene	Methyl Ethyl Ketone
Chloroform	Methyl Isobutyl ketone
Cyclohexane	Methyl Mercaptan
1,2-Dibromoethylene	Perchloroethylene
1,2-Dichloroethane	Propane
1,1-Dichloroethylene	Propylene
1,2-Dichloropropane	Propylene Oxide
EPA Method 25 Audit Gas[a]	Toluene
Ethylene	Trichloroethylene
Ethylene Oxide	Vinyl Chloride
Freon 113	

[a]Mixture of aliphatics, aromatics, and carbon dioxide.

Table II. Halocarbon Audit Cylinders Currently in Repository.

Compound	Low Concentration		High Concentration	
	No. of Cylinders	Concentration Range (ppm)	No. of Cylinders	Concentration Range (ppm)
Chloroform	2	5-20	2	300-700
1,2-Dichloroethane	4	5-20	4	100-600
Trichloroethylene	2	5-20	2	100-600
1,1-Dichloroethylene	2	5-20	2	100-600
Perchloroethylene	2	5-20	2	300-700
Vinyl Chloride	9	5-30	-	-------
Methylene Chloride	1	5-20	-	-------
Carbon Tetrachloride	1	5-20	-	-------
Freon 113	1	5-20	-	-------
1,1,1-trichloroethane	1	5-20	-	-------

Table III. Halocarbon Performance Audit Results.

Audit No.	Industry/ Source	Audit Material	RTI Measured Conc.(ppm)	Audit Result[a] Bias (Percent)
54	Research Program	Chloroform in N_2	16.5	NA[b]
		Chloroform in N_2	531	NA[b]
56	Reactivity of vent activated charcoal	Chloroform in N_2	8.11	NA[b]
68	EPA, Region II	Vinyl Chloride in N_2	5.74	NA[b]
		Vinyl Chloride in N_2	28.3	NA[b]
70	EPA, Region I	Vinyl Chloride in N_2	7.5	NA[b]
71	Degreasing vent	Trichloroethylene in N_2	14.9	-0.4
		Trichloroethylene in N_2	566	-8.7
74	Vinyl Chloride Production	1,2-Dichloroethane in N_2	9.30	+6.0
		1,2-Dichloroethane in N_2	462	+3.7

[a] Audit Result Bias = 100 X $\frac{\text{Client-Measured Conc. - RTI-Measured Conc.}}{\text{RTI-Measured Conc.}}$

[b] NA = Not Analyzed by client

Table IV. Analytical Errors

Compound	Total Variance	Variance Associated With:	
		Calibration	Measurement Error
Carbon tetrachloride	1.14	0.49	0.02
Freon 113	0.071	0.06	0.004
1,1,1-trichloroethane	0.31	0.05	0.003
Methylene chloride	0.18	0	0.007

Table V. Stability Study Results

Compound	No. of Cylinders	Number of[b] Measurements	Slope $\pm \sigma$, PPM/Day	Significant[a]
Chloroform	4	15	0.0018±0.0154	No
Perchloroethylene	4	12	0.1180±0.2922	No
1,2-Dichloroethane	8	42	-0.002±0.012	No
Trichloroethylene	4	20	-0.0004±0.008	No
1,1-Dichloroethylene	4	18	-0.006±0.010	No
Carbon Tetrachloride	1	7	-0.008±0.008	No
Freon 113	1	6	0.0001±0.004	No
1,1,1-trichloroethane	1	6	-0.003±0.006	No
Methylene chloride	1	7	0.003±0.003	No

[a]The change in concentration with time is significant if the mathematical range of (slope minus 2) to (slope plus 2) does not include the value of zero.

[b]Individual measurements found in Reference 1.